

Spin multiplicity and entanglement swapping in radical ion recombinations

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Abstract. We address the problem of relative frequencies of singlet and triplet recombinations in a multiparticle system, which consists of spin-correlated radical ion pairs. The nonlocal swapping of spin correlations due to cross-recombinations is taken into account. It is shown that this swapping does not contribute to singlet and triplet recombination frequencies in the absence of spin evolution in the correlated pairs.

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1. Introduction

The track created by a swift particle in a medium has a rather complicated structure, which depends on the type and energy of the particle [1]. This is due to specific processes of particle energy loss in the course of its collisions with molecules in the medium. Several radical ion pairs can be born in the same spatial region. These particles can then undergo either geminal recombination (within the initial pair) or cross-recombination. All geminal pairs are initially in their singlet spin state (Figure 1). The multiplicity of the pair can be changed by spin interactions with nuclei in the molecules and with external magnetic fields. The recombination probability per se is not affected by the multiplicity of the pair, but only singlet recombination normally leads to luminescence. Hence, external magnetic fields can influence the intensity of the recombination luminescence [2]. Investigation of this influence can provide important information on the structure of the radical ions, chemical processes which the radicals are involved in, and the structure of the radiation track [3, 4].

It is generally believed that the intensity of luminescence arising from cross-recombinations is not affected by magnetic field, since the spins of the particles are not initially correlated and, consequently, the probability of singlet recombination is universally equal to 1/4. This is supported by experiments on magnetic field effects in recombination luminescence induced by various sources of ionizing radiation [5]. The magnitude of the effect tends to decrease as the track density increases and, consequently, the fraction of cross-recombinations grows higher. Nevertheless, the question on the exact absence of magnetic

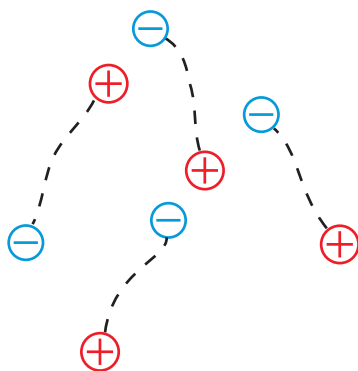


Figure 1. (Color online) The set of geminal pairs (connected with dotted lines). All the pairs are in their singlet spin state.

effects in cross-recombinations is still open. Some doubts are brought by magnetic field effect on alkane solutions irradiated with helium ions of 20 MeV [6]. Thus created tracks are extremely dense, which leads to a great number of cross-recombinations. Still a small magnetic effect has really been detected.

The magnetic effect in cross-recombinations can hypothetically be caused by a non-local quantum phenomenon related to the effect known in quantum information theory as entanglement swapping [7]. Brocklehurst was the first (even before the appearance of [7]) to pay attention to this phenomenon [8]. Its essence is as follows. Let there be no spin evolution in the geminal pairs. Then each geminal pair is in its singlet spin state for the period of time up to cross-recombination of any of its member. After the singlet cross-recombination of the fragments $\{2, 3\}$ of two singlet geminal pairs $\{1, 2\}$ and $\{3, 4\}$ the remaining pair of fragments $\{1, 4\}$ appears to be in the singlet state. This follows from the conservation of the total zero spin of the four particles. Note that the *a priori* (before the recombination of the radicals 2 and 3) spin state of the pair $\{1, 4\}$ was maximally mixed and, naturally, demonstrated no spin correlation. In such a manner the entanglement contained in the singlet state has been swapped inside the quadruple $\{1, 2, 3, 4\}$ from the couples $\{1, 2\}$ and $\{3, 4\}$ to the new ones $\{2, 3\}$ and $\{1, 4\}$. The first of these new pairs is the product of recombination and quits the subsequent consideration. The pair $\{1, 4\}$ continues its life in the medium. It can take part in a new act of entanglement swapping due to cross-recombination. Otherwise upon meeting of its fragments it will disappear in singlet recombination with unity probability. It is worth noting for the following that this unity probability is conditioned by the previous recombination of the pair $\{2, 3\}$.

Now let us suppose that the event of triplet recombination of the pair $\{2, 3\}$ took place and we know nothing about the orientation and alignment of the product. This is the situation of its isotropic triplet state. The same reasoning brings us to the conclusion that the pair $\{1, 4\}$ is also in the isotropic triplet state. This state is not entangled and only contains classical spin correlations, which are the result of swapping and transformation of the former singletness of the pairs $\{1, 2\}$ and $\{3, 4\}$. The meetings and recombinations of the fragments of the triplet pairs induce further spin correlation swapping (with the accompanying transformation) into

the remaining pair, etc.

Note that a non-local chemical reaction takes place when a spatially-separated pair of radicals in a definite spin state appears as a result of the distant recombination. It was shown in [9] that the swapping process significantly affects the spatial correlations of the recombination events.

The role of swapping of interparticle spin correlations in the relative frequencies of singlet and triplet recombinations seems to be important. Suppose that the swapping does affect the relative frequencies. By this way spin evolution in magnetic fields can modify the frequencies. We shall show that under certain conditions the swapping process does not manifest itself in the triplet and singlet recombination frequencies.

2. Model

We assume that no spin evolution takes place between the events of creation and recombinations. We then introduce the spin statistical operator $\hat{\varrho}_{a,b}$ for the pair of radicals with numbers a and b . This operator acts in the tensor product $\mathcal{H}_a \otimes \mathcal{H}_b$ of spin Hilbert states of the particles. We also need the following enumerable set of statistical operators labeled with the parameter $n = 0, 1, \dots$:

$$\hat{\varrho}_{a,b}^{(n)} = \frac{1}{4} \left[\hat{\sigma}_0(a) \otimes \hat{\sigma}_0(b) - \left(-\frac{1}{3} \right)^n \hat{\sigma}_k(a) \otimes \hat{\sigma}_k(b) \right]. \quad (1)$$

Here $\hat{\sigma}_0$ is the unit matrix 2×2 ; $\hat{\sigma}_k$ are Pauli matrices, k is the spatial axis index (x, y or z ; the summation over repeated indices is assumed). One can readily check that $\hat{\varrho}^{(0)}$ is the singlet state and $\hat{\varrho}^{(1)}$ is the isotropic triplet state. The set $\{\hat{\varrho}^{(n)}\}_{n=0}^{\infty}$ includes all the pair spin states which can appear in the course of recombinations and swapping process. To prove this we introduce the swapping map $S_{2,3}$ from the set of quadruple spin states to the set of the states of the couple $\{1, 4\}$ under the condition of singlet recombination of radicals 2 and 3, which initially belong to correlated pairs $\{1, 2\}$ and $\{3, 4\}$ [10]:

$$S_{2,3} : \hat{\varrho}_{1,2,3,4}^{(pre)} = \hat{\varrho}_{1,2} \otimes \hat{\varrho}_{3,4} \mapsto \hat{\varrho}_{1,4}^{(post)}. \quad (2)$$

The event of singlet recombination is equivalent to the positive result of an experiment checking the singlet status of the pair $\{2, 3\}$. Hence, we have

$$\hat{\varrho}_{1,4}^{(post)} = \frac{Tr_{2,3} \hat{\varrho}_{2,3}^{(0)} \hat{\varrho}_{1,2,3,4}^{(pre)}}{Tr_{1,2,3,4} \hat{\varrho}_{2,3}^{(0)} \hat{\varrho}_{1,2,3,4}^{(pre)}}. \quad (3)$$

It is easy to show that the map \mathcal{S} has the following simple realization in the set $\{\hat{\varrho}^{(n)}\}_{n=0}^{\infty}$ (Figure 2):

$$\mathcal{S}_{2,3} : \hat{\varrho}_{1,2}^{(n)} \otimes \hat{\varrho}_{3,4}^{(m)} \mapsto \hat{\varrho}_{1,4}^{(n+m)}. \quad (4)$$

In a similar way we introduce the map for the case of (isotropic) triplet recombination of the pair $\{2, 3\}$:

$$\mathcal{T}_{2,3} : \hat{\varrho}_{1,2,3,4}^{(pre)} = \hat{\varrho}_{1,2} \otimes \hat{\varrho}_{3,4} \mapsto \frac{Tr_{2,3} [\hat{\sigma}_0(2) \otimes \hat{\sigma}_0(3) - \hat{\varrho}_{2,3}^{(0)}] \hat{\varrho}_{1,2,3,4}^{(pre)}}{Tr_{1,2,3,4} [\hat{\sigma}_0(2) \otimes \hat{\sigma}_0(3) - \hat{\varrho}_{2,3}^{(0)}] \hat{\varrho}_{1,2,3,4}^{(pre)}}. \quad (5)$$

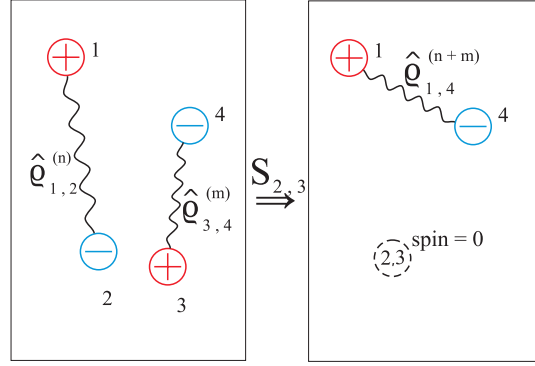


Figure 2. (Color online) The swapping of spin correlations in the course of *singlet* recombination of particles 2 and 3. The dotted circle represents the product of recombination.

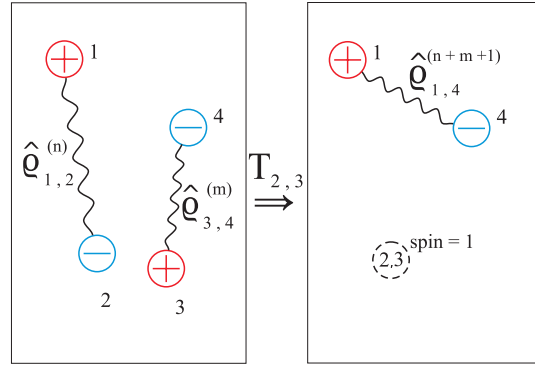


Figure 3. (Color online) The swapping of spin correlations in the course of *triplet* recombination of particles 2 and 3.

In the set $\{\hat{\varrho}^{(n)}\}_{n=0}^{\infty}$ one gets (Figure 3):

$$\mathcal{T}_{2,3} : \hat{\varrho}_{1,2}^{(n)} \otimes \hat{\varrho}_{3,4}^{(m)} \mapsto \hat{\varrho}_{1,4}^{(n+m+1)}. \quad (6)$$

We see that if only singlet and triplet pairs are created in the medium by irradiation, the swapping maps \mathcal{S} and \mathcal{T} generate the entire set $\{\hat{\varrho}^{(n)}\}_{n=0}^{\infty}$ of the spin states.

Let $f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)$ be the density of pairs in the spin state $\hat{\varrho}^{(n)}$ and with locations of radicals near the points \mathbf{r}_1 and \mathbf{r}_2 . The first partner in every pair is the radical of the type “+”, and the second – of the type “-”. Recombinations take place only between partners of different types. We also introduce the radical spatial densities $g_+(\mathbf{r}) = \sum_{n=0}^{\infty} \int f^{(n)}(\mathbf{r}, \mathbf{r}') d^3\mathbf{r}'$ and $g_-(\mathbf{r}) = \sum_{n=0}^{\infty} \int f^{(n)}(\mathbf{r}', \mathbf{r}) d^3\mathbf{r}'$, which can readily be obtained from $f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)$. These notions let us introduce the following important operator $\langle \hat{\varrho}(\mathbf{r}_1, \mathbf{r}_2) \rangle$, which is the average spin state of a “+–”-pair, localized at the points \mathbf{r}_1 and \mathbf{r}_2 :

$$\langle \hat{\varrho}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{1}{4} \left(1 - \sum_n \frac{f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)}{g_+(\mathbf{r}_1)g_-(\mathbf{r}_2)} \right) \hat{\sigma}_0 \otimes \hat{\sigma}_0 + \sum_n \frac{f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)}{g_+(\mathbf{r}_1)g_-(\mathbf{r}_2)} \hat{\varrho}^{(n)}. \quad (7)$$

The first term is the maximally mixed state with the proper weight $\hat{\sigma}_0 \otimes \hat{\sigma}_0/4$. This is the case when the pair was neither geminal, nor created in the swapping process. The second term reflects the contribution of situations when the pair appears to be correlated due to some sequence of swapping acts.

The expression for $\langle \hat{\rho}(\mathbf{r}_1, \mathbf{r}_2) \rangle$ has the following simple form:

$$\langle \hat{\rho}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{1}{4} \left[\hat{\sigma}_0 \otimes \hat{\sigma}_0 - \xi(\mathbf{r}_1, \mathbf{r}_2) \hat{\sigma}_k \otimes \hat{\sigma}_k \right], \quad (8)$$

where

$$\xi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{n=0}^{\infty} \left(-\frac{1}{3} \right)^n \frac{f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)}{g_+(\mathbf{r}_1)g_-(\mathbf{r}_2)}. \quad (9)$$

If we average the parameter $\xi(\mathbf{r}, \mathbf{r})$ over the volume of the system, we get the weights of singlet and triplet states of every meeting pair and, consequently, the relative frequencies of singlet and triplet recombinations.

Evaluation of the parameter $\xi(\mathbf{r}, \mathbf{r})$ requires an explicit form of kinetic equation for $f^{(n)}(\mathbf{r}_1, \mathbf{r}_2)$. We take the following model system:

$$\begin{aligned} \partial_t f^{(n)}(\mathbf{r}_1, \mathbf{r}_2) = & -\kappa(g_-(\mathbf{r}_1) + g_+(\mathbf{r}_2))f^{(n)}(\mathbf{r}_1, \mathbf{r}_2) + \\ & + \frac{\kappa}{4} \sum_{m=0}^n \int f^{(m)}(\mathbf{r}_1, \mathbf{r}) f^{(n-m)}(\mathbf{r}, \mathbf{r}_2) d^3\mathbf{r} + \\ & + \frac{3\kappa}{4} \sum_{m=0}^{n-1} \int f^{(m)}(\mathbf{r}_1, \mathbf{r}) f^{(n-m-1)}(\mathbf{r}, \mathbf{r}_2) d^3\mathbf{r} + \\ & + (D_+ \Delta_{\mathbf{r}_1} + D_- \Delta_{\mathbf{r}_2}) f^{(n)}(\mathbf{r}_1, \mathbf{r}_2) + \gamma^{(n)} w(|\mathbf{r}_1 - \mathbf{r}_2|). \end{aligned} \quad (10)$$

The first term in the r.h.s. is the loss of pairs because of recombination of one of its fragments; κ is the recombination rate. The second and third terms stand for the creation of a new pair due to swapping act caused by singlet and triplet recombination, respectively (the recombination takes place at the point \mathbf{r}). We assume that the cross-sections of the singlet and triplet recombinations are equal (as in the case of charged radicals). Under these conditions the factors 1/4 and 3/4, with which the recombination constant appears in these terms, are stipulated by the weights of singlet and triplet states in the maximally mixed spin state (this is the state of the meeting pair of radicals – fragments of different correlated pairs). The summation over m reflects the laws (4) and (6) of spin state transformation in the course of swapping. The last line contains the diffusion terms and the gain term due to ionization; the parameter $\gamma^{(n)}$ is the generation rate (we assume that only $\gamma^{(0)}$ and $\gamma^{(1)}$ are non-zero); the form-factor $w(r)$ gives the distribution of the relative positions of the created radicals.

3. Results and Discussion

Under the homogeneous spatial conditions the densities g_+ and g_- are identical and do not depend on coordinates. At the same time the pair density is a function of the distance between the constituents. Upon multiplication of (10) by $(-1/3)^n g^{-2}$ and summation over n one gets

$$\partial_t \xi(r) = -2\kappa g \xi(r) + (D_+ + D_-) \Delta_{\mathbf{r}} \xi(r) + \frac{\gamma^{(0)} - \gamma^{(1)}/3}{g^2} w(r). \quad (11)$$

The main point is the annihilation of the terms in (10) responsible for the swapping process. Hence this process makes no contribution to the evolution of $\xi(r)$. This means that under the

absence of intermediate spin evolution the swapping does not affect the relative frequency of singlet and triplet recombinations. Note that the validity of this conclusion does not depend on the form of the migration terms in the kinetic equation (10) (the diffusion terms we used are not the best possible approximation).

As has already been mentioned, the parameter $\xi(r)$ for $r = 0$ lets one evaluate the ratio of the frequencies of the singlet (ν_S) and triplet (ν_T) recombinations:

$$\frac{\nu_S}{\nu_T} = \frac{1 + 3\xi(0)}{3 - 3\xi(0)}. \quad (12)$$

It should be stressed that in the ratio (12) we take into account all the recombinations – between uncorrelated radicals as well as between the fragments of a correlated pair. On the contrary, only the recombinations of the first type should be considered in the equation (10).

4. Conclusions

The main result of the work is the conclusion that the swapping process in the absence of spin evolution does not affect the relative frequencies of singlet and triplet recombinations. For instance, there is no spin evolution in the case of zero hyperfine interaction between electrons and nuclei in radicals and equal g -factors for radical cation and anion. This result may be considered as an argument in support of the present approaches to the evaluations of magnetic field effects, neglecting any possible magnetic influence on cross-recombinational luminescence. Nevertheless, a more accurate analysis with an explicit account of spin evolution and temporal dependencies of singlet and triplet recombination probabilities is required for description of a pulsed experiment.

Acknowledgments

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